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(54) Title: A LUBRICATING METHOD FOR SILICATE DRILLING FLUIDS

(57) Abstract

Improved silicate drilling fluids are produced by the addition of tetra alkyl ammonium compounds, in particular tetra methyl ammonium hydroxide to silicate drilling fluid mud to lower the co-efficient of friction between drill string and wellbore. It has also been discovered that the same tetra alkyl ammonium lubricant compounds greatly lessen the viscosity breakdown of swelled hectorite clay in the presence of silicate. This allows the preparation of silicate drilling fluids not only with enhanced lubricity but having stable rheology at the higher temperature and pressures encountered in some drilling operations.

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A LUBRICATING METHOD FOR SILICATE DRILLING FLUIDS

BACKGROUND OF THE INVENTION

5 This invention relates to novel silicate based drilling fluids to be used primarily in well drilling for oil and gas. In particular this invention concerns the formulation of a silicate based drilling fluid that provides greater lubrication during drilling and can be used as a high
10 pressure and high temperature rheology agent

The use of silicate as a drilling fluid component is well established. Silicate has been used since the 1930's as an effective means of stabilizing shale formations.
15 Despite being an effective shale stabilizer, silicate never achieved early, widespread success, owing to certain advantages held by oil based drilling fluids. Oil based drilling fluids offer ease of use, are not prone to gellation or precipitation and provide good lubrication between the drill string and well bore, as measured by coefficients of friction in the range of 0.10 to 0.18 compared with a range of 0.18 to 0.22 for water-based fluids. Until recent environmental pressures there was little incentive to improve the performance deficiencies in
20 silicate-containing, water-based drilling fluids.
25

The first aspect of this invention deals with improving the lubricating properties of silicate by the addition of a lubricant which remains effective in highly alkaline
30 silicate media. Good lubrication is necessary in order to avoid slower drilling rates, differential sticking, higher torque, fatigue on the drill string and possible hole loss. These problems become more acute with increases in hole length or the hole angle.
35

We have discovered that the addition of certain tetra alkyl ammonium compounds, in particular tetra (lower alkyl)

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ammonium hydroxide, to silicate or silicate drilling fluid mud can lower the co-efficient of friction between the drill string and well bore. As well as meeting lubricant requirements, tetra alkyl ammonium compounds are
5 environmentally safe, compatible with other drilling additives and temperature and time stable.

The second aspect of this invention deals with
10 imparting stable high pressure and high temperature (HPHT) rheology to a silicate drilling fluid. The rheology of a drilling fluid is a critical factor governing such drilling characteristics as removal of drill cuttings, stabilization of the rock formation, ease of pumping, control of fluid loss and drill string support. It is critical that a
15 desirable rheology be maintained during the full range of temperatures encountered during the drilling procedure. Maintenance of rheology becomes increasingly difficult as higher temperatures are encountered downhole.

20 Although silicate itself is stable at HPHT, the viscosity increasing organic polymeric additives typically used to impart rheological properties and to control fluid loss are by themselves subject to breakdown at HPHT. We have discovered that the combination of the aforementioned
25 tetra alkyl ammonium compounds with silicate and, additionally, a hectorite clay, results in a useful, HPHT-stable rheology for drilling. It is believed that other applications in which control of rheology is important, such as coatings and adhesives, might well benefit from the
30 discovery of this synergic enhancement of properties, quite apart from the specific present application of rheology agents for drilling fluids.

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Swelling clays such as bentonite are used extensively in the drilling fluid industry as rheology agents. As well as providing a useful rheology, swelling clays are resistant to HPHT. Swelling clays had not been used with silicate-based drilling fluids, however, because the addition of a small amount of silicate to a swelled clay often results in total loss of viscosity of the swelled clay. That loss of viscosity or rheological properties is due to the dispersion effect silicate has on clay platelets.

10

Swelled hectorite clay, on the other hand, apparently can retain partial viscosity after the addition of silicate, with the loss of viscosity in a swelled hectorite clay proportional to the amount of silicate added. We have discovered that inclusion of a tetra alkyl ammonium compound reduces the dispersion effect of silicate has on the swelled hectorite, thus allowing for a greater range of formulating hectorite with silicate in drilling fluids.

20

A further advantageous effect of the addition of tetra alkyl ammonium hydroxide to silicate-based drilling fluids containing hectorite clays is that the resulting modification to the rheology and the silicate/clay mud produces a drilling fluid more comparable in behavior, in low- to medium-pressure and temperature wells, to conventional organic gum systems which are subject to decomposition at HPHT.

25

SUMMARY OF THE INVENTION

With a view to providing a silicate-based drilling fluid exhibiting good lubricity in oil- and gas-drilling applications, there is provided a silicate drilling fluid

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comprising 50 to 95 percent parts per volume (ppv) water; 5
to 50 percent ppv silicate and 0.1 to 15 percent ppv tetra
alkyl ammonium compounds. Because both the silicate and the
tetra alkyl ammonium compounds which are components in
drilling fluids according to the present invention are
available either in the form of solids or aqueous solutions,
concentration units of "percent parts per volume" are used,
to indicate the number of grams (for solid components) or
milliliters (for liquid components) of the component which
has been added in making up 100 milliliters of drilling
fluid in the final composition.

The preferred tetra alkyl ammonium compound is ammonium
hydroxide tetrasubstituted with lower alkyl (methyl to
butyl) groups. The currently preferred compound is
tetramethylammonium hydroxide (TMAH).

Silicates useful in carrying out the present invention
include materials in solution as well as hydrated solids and
anhydrous silicates exhibiting molar ratios of SiO₂:Na₂O
(and/or K₂O) in the range of 1.5 to 4.0. A particular
silicate which has been found useful in silicate-based
drilling fluids according to the present invention is D
Sodium Silicate (trademark) manufactured by the PQ
Corporation (Valley Forge, Pennsylvania). D® Sodium
Silicate exhibits a weight ratio of SiO₂:Na₂O of about 2.0.

It is preferred to prepare silicate-based drilling
fluids according to the present invention by adding the TMAH
lubricant to the silicate mud, i.e., to the pre-mixed
water/silicate. In that way the higher levels of lubricant
in the silicate drilling fluid can be achieved, compared
with the procedure of pre-mixing the lubricant with silicate
before adding the water. TMAH and other tetra alkyl

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ammonium compound lubricants of the kind comprehended in the present invention are not as soluble in liquid silicate as in a water-diluted silicate drilling fluid. Nevertheless, we have discovered that the lubricant is effective at low 5 concentrations.

With a view to formulating a silicate mud having a stable rheology at high pressure and high temperature, there is added to a silicate-based drilling fluid continuing the 10 tetra alkyl ammonium compound lubricants, a suitable amount of a hectorite clay. To provide HPHT rheology, we have found that hectorite clay in the amount of 1-10 percent ppv should be included in the final formulation.

15

BRIEF DESCRIPTION OF THE DRAWING

The single drawing, Figure 1, is a graphic presentation 20 of data comparing the coefficient of metal-metal friction for different drilling fluids.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

In the experimental examples given below, the silicate used in formulating silicate drilling fluids according to the present invention is D® Silicate manufactured by PQ Corporation. TMAH and tetrabutylammonium hydroxide (TBAH) were obtained as 25 percent aqueous solutions manufactured 30 by Sachem (Cleburne, Texas).

"Hectorite clay" refers to a subset of the smectite or swelling clays, differing from the others in being composed primarily of sodium magnesium lithium silicate and in

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exhibiting a smaller platelet size. A form of hectorite which has been found particularly useful in Bentone EW (trademark) manufactured by the Rheox Corporation (Highstown, New Jersey).

5

Following the standard used in the drilling industry, liquid components such as water or silicate are measure by volume. Solid material such as rheology agents are measured by weight. The 25% dissolved solution of TMAH was used
10 during testing. TMAH levels are reported on a "as used" basis.

15

Example 1

20 Example #1 illustrates the drop in coefficient of friction (i.e., enhanced lubricity) achieved with a lubricant (TMAH or TBAH) has been post-added to a silicate drilling fluid.

The silicate drilling fluid was prepared according to the illustrated formulation and served as a control and a
25 base fluid for the addition of the lubricant. All compositions in this example were manufactured by first metering-in the viscosity-increasing rheology agents (xantham gum and polyanionic cellulose) into water under moderate agitation. Sufficient time was allowed for the rheology agent to develop viscosity. The next was either adding the silicate followed by the lubricant or adding
30 silicate/lubricant that had been pre-blended. Lubricity was measured using a Baroid™ Combination EP (extreme pressure) and lubricity test meter. The control formulation consisted

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of:

1. 70 pbv water
2. 0.43 pbw xantham gum (Kelzan XCD)
3. 0.43 pbw polyanionic cellulose (Staflo Exlo Supreme)
4. 30 pbv sodium silicate (D®)

Lubricants evaluated were tetramethylammonium hydroxide TMAH (25% solution in water) and tetrabutylammonium hydroxide TBAH (25% solution in water)

Table 1: Lubricity Results

Formulation	lubricant post added (pbv to pbv silicate)	co-efficient of friction
Water	0	0.340
Control	0	0.391
Control	0.5% TMAH	0.342
Control	1.0% TMAH	0.301
Control	5.0% TMAH	0.305
Control	10.0% TMAH	0.307
Control	5.0% TBAH	0.341

The addition of 1.0 percent TMAH to the control silicate-base fluid reduced the coefficient by 23 percent.

Example 2

In the formulation tested, lubricant was pre-added to the silicate and then formulated to make a silicate drilling fluid. Lubricity testing was switched to an HLT Lubricity Tester. The HLT lubricity tester consists of a metal test bob 3 inches in length and 2.5 inches in diameter. The bob is rotated in a metal pipe with the drilling fluid that is being tested being circulated at a constant flow rate. It was believed that this test protocol better matched conditions that would be met during drilling.

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Formula

1. 70 pbv water
2. 0.43 pbw xantham gum (Kelzan XCD)
3. 0.43 pbw polyanionic cellulose (Staflo Exlo Supreme)
4. 30 pbv D® silicate premixed (a) 1.0% pbv TMAH to silicate; or
5. 5.0% pbv TMAH to silicate

Table 2 shows the reduction of the average co-efficient of friction while Figure 1 shows the initial co-efficient of friction and the rate of decrease to the average co-efficient of friction. The initial friction and rate of friction drop are critical since these have a direct bearing on torque requirements and metal strength.

Table #2

Formulation	Amount TMAH present (pbv TMAH to pbv silicate)	Average co-efficient of friction
Water	0	0.39
Control from example #1	0	0.23
Example #2a	1.0% TMAH	0.16
Example #2b	5.0% TMAH	0.15

25

Example #3

In this example, the rheological properties of various combinations of water, hectorite clay (Bentone EW), Silicate D and TMAH (25 percent aqueous solution) are presented in Table 3a.

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The data illustrate the thinning effect which added silicate has on swelled hectorite in water and the offsetting thickening effect when TMAH is mixed into the silicate prior to the addition of the silicate to swelled 5 hectorite in water. TMAH was seen to have a thinning effect when silicate was not present.. There was an observed tendency of all of the fluids to increase in viscosity after hot rolling, which is believed to be the result of better setting of the hectorite clay with time, agitation and heat.

10

Rheology measurements were made using an OFI 8-speed Model 100 viscometer, with all rheology measurements taken at 120°F, following API recommended practice (Guide 13B-1, section 2). Rheology testing was carried out both before 15 and after hot roll aging. Hot roll aging was carried out at 300°F for 16 hours, in accordance with the recommended practices of API Manual 13I, section 19.

20

By way of comparison, the rheology profile of the control of Example No. 1, supra, is shown in Table 3b below.

25

30

In practice, in formulating drilling fluids for use in the field, the independent variable will be the silicate loading. Thus, in Examples 1 to 3, the silicate loading is 30 percent. Rheology measurements can then be carried out varying the dependent variables of the relative amounts added of tetra alkyl hydroxide lubricant compounds and hectorite clay, to optimize the rheological behavior. In Example No. 5 discussed below, a silicate loading level of 15 percent is used in the drilling fluid formulations tested.

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Table #3a: Hectorite Formulations

	1	2	3	4			
Water	1000 pbv	1000 pbv	700 pbv	700 pbv			
Bentone®	40 pbw	40 pbw	40 pbw	40 pbw			
EW							
D®	0	0	300 pbv	300 pbv			
silicate							
TMAH (25%)	0	3 pbv	0	3 pbv			
Rheology prior to Hot Rolling							
600 rpm	103	94	34	125			
300 rpm	83	69	20	125			
200 rpm	60	54	15	124			
100 rpm	46	40	10	91			
6 rpm	21	15	5	51			
3 rpm	16	12	5	48			
10 s gel	18	15	5	48			
10 min gel	26	25	5	54			
Rheology After Hot Rolling for 16hrs @ 300°F							
600 rpm	158	100	40	225			
300 rpm	152	82	22	211			
200 rpm	140	78	16	198			
100 rpm	131	72	10	184			
6 rpm	108	60	5	97			
3 rpm	96	47	5	85			
10 s gel	78	44	5	78			
10 min gel	82	48	5	75			

Table 3b: Rheology profile of example #1, control

	600 rpm	300 rpm	200 rpm	100 rpm	6 rpm	3 rpm	10 s gel	10 min gel
Not hot rolled	60	42	35	25	9	6	8	12
Hot rolled	8	4	2	1	0	0	0	0

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Example 4

This example illustrates the interaction of hectorite (Bentone® EW) and TMAH (25% aqueous solution) at silicate (D°) fixed at 30% pbv. The silicate concentration was set at 30% pbv because this was believed to be a level of silicate that would be both highly inhibitive of shale and stable from possible problems associated with acidic gases and multivalent cation contamination coming from the bore hole.

A central composite experimental design was used to characterize the interaction of hectorite (Bentone[®] EW) and TMAH (25% aqueous solution) at silicate (D[®]) fixed at 30% pbv. The TMAH was mixed with the silicate prior to adding the silicate/TMAH to the swelled hectorite clay. The factors for the central composite design were set such that the rheology response would provide a range of results that could be deemed useful for drilling fluids. For those familiar with central composite experimental designs, the factors are shown in Table 4a.

Table 4a: Experimental Variables

Factor	-	+
Bentone® EW	2.5% pbw	3.5% pbw
TMAH (25% solution)	1.0% pbv to silicate	2.0% pbv to silicate

Table 4b: Formulations vs. Rheology

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silica te	ml	ml	ml	ml	ml	ml	ml	ml	ml	ml	ml	ml	ml
TMAH*	3ml	3ml	6ml	6ml	4.5 ml	4.5 ml	2.3 7ml	6.6 3ml	4.5 ml	4.5 ml	4.5 ml	4.5 ml	4.5 ml
PRIOR TO HOT ROLLING													
600 rpm	54	120	54	63	46	105	60	63	58	60	62	58	
300	36	112	33	40	28	103	53	35	51	55	51	38	
200	26	110	23	34	20	82	40	26	41	48	40	32	
100	17	110	11	25	15	69	34	16	35	42	30	28	
6	8	55	3	10	5	30	16	5	16	25	13	12	
3	5	41	2	7	3	30	10	4	10	16	8	9	
10s gel	7	44	3	8	5	31	11	5	10	12	8	10	
10min gel	7	59	3	9	5	28	11	5	11	12	6	10	
AFTER HOT ROLLING 16 HRS @ 300°F													
600 rpm	58	90	50	67	44	70	63	46	59	57	65	50	
300	33	84	29	48	26	66	58	28	54	52	52	31	
200	29	82	22	39	19	59	49	20	41	45	42	28	
100	21	81	12	28	14	53	41	11	34	38	32	22	
6	6	44	5	12	5	25	19	4	17	20	13	12	
3	4	36	4	10	3	17	12	2	10	11	8	8	
10 s gel	5	38	4	10	4	22	15	3	10	12	9	9	
10s min	6	40	4	11	4	23	15	3	10	13	10	10	

30

Example #5

35

This example illustrates the effect of increasing the TMAH dosage from 0 (column no. 1) in stages up to 0.35 percent ppv (column no. 4). In the formations given in this example, the TMAH has been post-added to a silicate/hectorite drilling fluid (silicate loading 15 percent).

40

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Table 5: Formulations vs. Rheology

	#1	#2	#3	#4	
FORMULATIONS					
5	Water	850 ml	850 ml	850ml	850ml
10	Bentone® EW	40g	40g	40g	40g
15	D® silicate	150ml	150ml	150ml	150ml
20	TMAH*	0	1.5ml	2.63ml	3.75ml
25	PRIOR TO HOT ROLLING				
30	600 rpm	29	55	102	133
35	300	23	42	83	135
40	200	19	36	62	148
45	100	17	26	50	146
50	6	12	11	36	85
55	3	8	9	33	66
60	10s gel	8	10	25	60
65	10min gel	10	19	36	64
70	AFTER HOT ROLLING FOR 16HRS AT 300F				
75	600 rpm	37	53	112	232
80	300	25	42	95	198
85	200	22	37	82	180
90	100	19	29	64	158
95	6	13	17	44	88
100	3	8	11	38	67
105	10 s gel	9	15	40	67
110	10s min	10	16	44	72

CONCLUSION

Novel silicate-based drilling fluid compositions have been achieved which afford improved lubrication between the drill string and well bore, through the addition of lubricant compounds selected from the group of tetra- (lower alkyl) ammonium hydroxide compounds.

Additionally, the inclusion of added hectorite clay to drilling fluids according to the present invention affords rheological stability at high-temperature, high-pressure

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drilling conditions. This is a surprising result, in that swelling clays such as Bentonite are known to lose viscosity in the presence of silicate. The tetra alkyl ammonium compounds used in lubricants in drilling fluids according to
5 the present invention significantly reduce the "dispersion" effect of silicate on swelled hectorite, thus allowing for a much greater range of formulations of drilling fluid for use at all temperature and pressure conditions encountered in the working of an oil or gas well.

10

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CLAIMS:

1. A silicate fluid for drilling a wellbore, comprising water, silicate, a viscosity-increasing material and as a lubricity-enhancing agent, from 0.1 to 15% ppv of a tetra-(lower alkyl) ammonium hydroxide.
5
2. A silicate drilling fluid as in claim 1, wherein said tetra-(lower alkyl) hydroxide is selected from tetra methyl ammonium hydroxide (TMAH) and tetra butyl ammonium hydroxide (TBAH).
10
3. A silicate drilling fluid according to claim 2, wherein said silicate exhibits a molar ratio of $\text{SiO}_2:\text{M}_2\text{O}$ in the range of 1.5 to 4.0 where M is Na or K, and said silicate makes up from 5 to 50% ppv of the drilling fluid composition.
15
4. A silicate drilling fluid according to claim 1, wherein said viscosity-enhancing material is a hectorite clay, present in an amount of from 1 to 10% ppv of the drilling fluid composition.
20
5. A silicate drilling fluid according to claim 1 or claim 4, wherein said tetra-(lower alkyl) hydroxide is TMAH or TBAH.
25
6. A silicate drilling fluid according to claim 4, wherein said silicate exhibits a molar ratio of $\text{SiO}_2:\text{M}_2\text{O}$ in the range of 1.5 to 4.0 where M is Na or K, and said silicate makes up from 5 to 50% ppv of the drilling fluid composition.
30
7. A method of preparing a water-based silicate drilling

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- 5 (a) preparing a base fluid by mixing a viscosity-increasing agent with water and, when the viscosity of said aqueous mixture has stabilized, adding from 5 to 50% ppv of a silicate exhibiting molar ratio of $\text{SiO}_2:\text{M}_2\text{O}$ in the range of 1.5 to 4.0 where M is Na or K; and
- 10 (b) adding to said aqueous mixture a lubricant selected from the group of tetra- (lower alkyl) hydroxides in a proportion of from 0.1 to 15% ppv.

8. A method of preparing a water-based silicate drilling fluid, comprising the steps of:

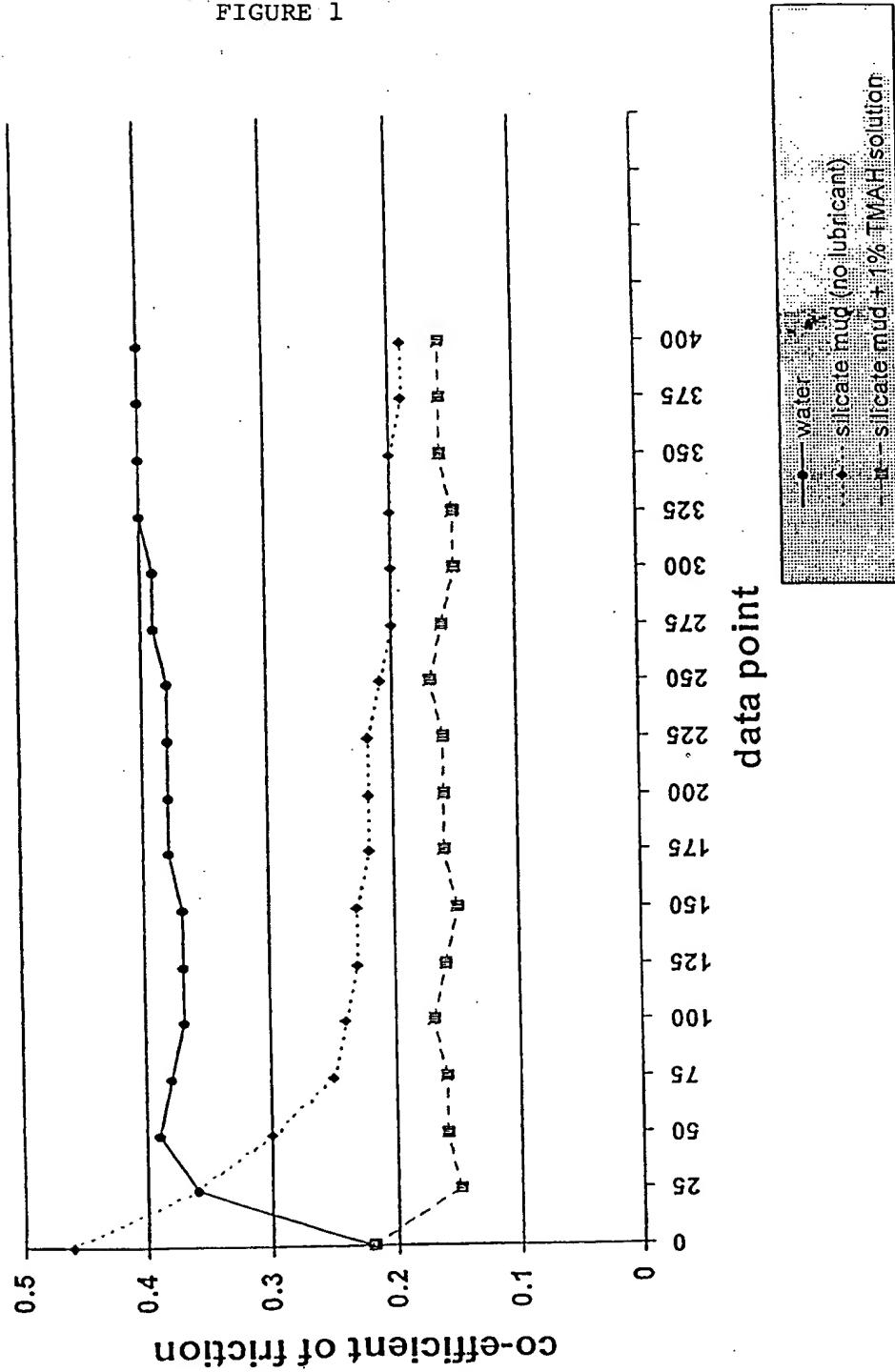
- 15 (a) preparing a base fluid by mixing a viscosity-increasing agent with water and allowing the mixture to stabilize; and
- 20 (b) adding a pre-blended solution of a tetra- (lower alkyl) hydroxide in an aqueous solution of a silicate exhibiting a molar ratio of $\text{SiO}_2:\text{M}_2\text{O}$ in the range of 1.5 to 4.0 where M is Na or K

25 to produce a drilling fluid composition comprising 50 to 95% ppv of water, 5 to 50% ppv of said silicate, and 0.1 to 15% ppv of said tetra- (lower alkyl) hydroxide.

- 30 9. A method according to claim 7 or claim 8, wherein said viscosity-increasing agent is a hectorite clay added in a proportion to make up from 1 to 10% ppv of the final drilling fluid composition.

1/1

FIGURE 1

Lubricity Test Results (metal to metal)

INTERNATIONAL SEARCH REPORT

Inten	nal Application No
PCT/CA 99/00596	

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09K7/00 C09K7/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09K E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 949 058 A (GROVES WILLIAM L ET AL) page 2, line 11 - line 53 page 2, line 75 page 4, line 75 - line 80	1-9
X	US 4 637 883 A (PATEL ARVIND D ET AL) 20 January 1987 (1987-01-20) column 3, line 41 - line 59; claims 1-10	1-9
X	EP 0 390 387 A (HALLIBURTON CO) 3 October 1990 (1990-10-03) page 3, line 3 - line 25; claims 1-9	1-9
X	US 5 380 706 A (HIMES RONALD E ET AL) 10 January 1995 (1995-01-10) claims 1-19; examples 1,2 page 4, line 47 - line 49	1-9

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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

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